CHROM. 8486

DETERMINATION OF TRACE IMPURITIES IN GASES BY THEIR EQUILIBRIUM ACCUMULATION IN VOLATILE LIQUIDS

B. V. IOFFE, A. G. VITENBERG, V. N. BORISOV and M. A. KUZNETSOV
Leningrad State University 199164 Leningrad (U.S.S.R.)

SUMMARY.

A brief discussion is given of work devoted to the theoretical substantiation and experimental testing of a new method for the determination of trace amounts of organic compounds in gases by their concentration in a suitable volatile solvent and subsequent injection into a chromatograph after equilibrium has been reached.

The method has substantial advantages over the known techniques of concentration of micro-amounts of impurities by adsorbents and non-volatile liquids, but its application is limited by the availability of a suitable solvent.

Results are presented that illustrate the determination of simple aromatic hydrocarbons, carbonyl compounds and diethylamine in air at the level of 0.1–65 mg/m³.

INTRODUCTION

The last 15 years have seen the successful application in gas chromatography of phase equilibria, involving the participation of the compound under study, which are established outside the chromatographic column, with the purpose of improving the selectivity or sensitivity of the analysis. There are already efficient methods for determining volatile compounds in liquid (and solid) solutions by means of gas chromatographic analysis of the vapour phase, the so-called head-space analysis (for a review, see ref. 1), and interesting work on the equilibrium concentration of impurities from gases in volatile liquids carried out by Janák and co-workers at the Czechoslovak Academy of Sciences[2–4] and by Dravnieks and Krotoszynsky at the Illinois Institute of Technology[5].

In this paper, we report some results obtained for the theoretical substantiation and experimental testing of a new type of equilibrium concentration applied to gaseous micro-impurities. Trace amounts of organic impurities in the atmosphere (and in other gases) can, in some instances, be determined successfully by saturating a comparatively volatile liquid with the gas under study until the components have reached an equilibrium distribution between the two phases. After equilibration, the liquid is injected directly into a chromatograph and the concentration of impurities in it determined.

This method of analysis has several advantages. For instance, when the parti-

tion coefficients are favourable, the sensitivity of the determination of micro-amounts of impurities can be improved by their accumulation in a liquid. Also, in instances when the partition coefficients of the components in a mixture under analysis are in a favourable ratio, improved selectivity is possible.

A further advantage of the method is the possibility of running repeated analyses on one sample and to preserve and despatch small sealed ampoules containing samples from the site of sampling to specialized analytical laboratories.

Furthermore, there is no need for the precise measurement of the volume of the absorbing liquid, or for separating impurities from the absorbing liquid (*e.g.*, by thermal desorption), since the inherent sources of error are completely removed. Thus the disadvantages of the traditional methods of concentration associated with the necessity for removal of water, for taking into account the amount of the gas passed and for preventing the compounds of interest from passing through the trap are removed.

Finally, there is the possibility of collecting and preserving samples of labile compounds that might otherwise change on coming into contact with the material of the equipment or as a result of oxidation.

The first two of the above advantages are common for all techniques of equilibrium concentration, while the other advantages are inherent in our version, which involves the use of fairly volatile absorbing liquids that are injected directly into the chromatograph in an analysis. These substantial advantages can, however, be realized only by the proper selection of the absorbing liquid, which should meet certain specific requirements. The limits of applicability of the proposed method of equilibrium concentration in volatile liquids can be established only by a theoretical consideration of the process of micro-impurity distribution when the polluted gas is passed through a pure liquid. The formulae derived for the equilibrium concentration in non-volatile liquids are completely inapplicable here, so that we had to develop a new mathematical description of the process[6]. The results obtained can be summarized as follows.

THEORETICAL

The formula describing the dynamics of the accumulation of impurity in a trapping liquid, taking into account its volatility, can be written as follows:

$$C_L = \frac{Kf}{1-AK} \cdot C_G \left[1 - \left(1 - A \cdot \frac{V_G}{V_L^0} \right)^{\frac{1-AK}{AK}} \right] \tag{1}$$

where C_L and C_G are the concentrations of the micro-impurity in the absorbing liquid and the gas to be analyzed, respectivily, K is the partition coefficient of the impurity, $f = (P - P_L)/P$ (P being external pressure and P_L the vapour pressure of the absorbing liquid at the temperature of the experiment), A is the volume of the absorbing liquid per unit volume of the gas saturated by it (representing a measure of the volatility of the liquid), V_G is the volume of the gas measured after its passage through the liquid and V_L^0 is the initial volume of the liquid.

The curves corresponding to this equation are shown in Fig. 1. These curves have different degrees of curvature with different signs depending on the magnitude
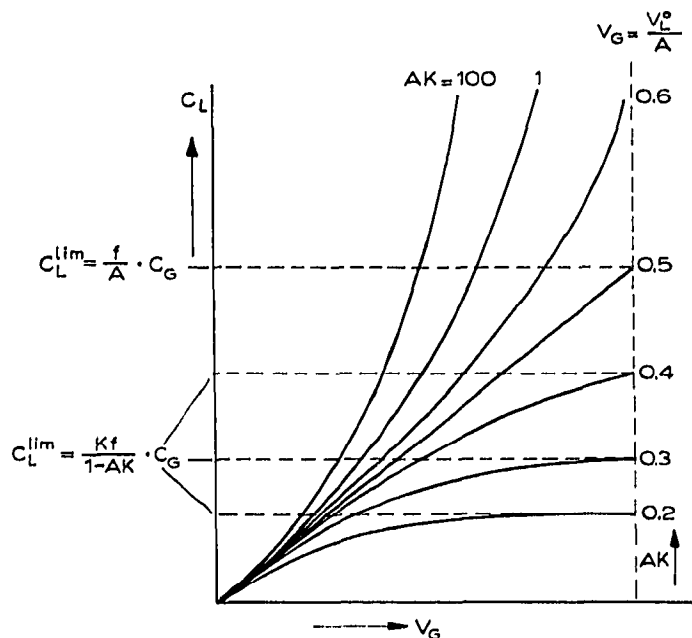
Fig. 1. Accumulation of micro-impurities in the course of equilibrium concentration in liquids with various values of AK.

of the product of the volatility of the liquid and the partition coefficient of the impurities:

(a) when $AK > 0.5$, the C_L *versus* V_G curves are concave, the derivative dC_L/dV_G tending to infinity at the moment of complete liquid evaporation;

(b) when $AK < 0.5$, the C_L *versus* V_G curves are convex, the derivative tending to zero.

The latter case is particularly important for analytical pruposes. Indeed, when $V_G \rightarrow V_L^0/A$, a steady-state concentration of impurities is established in the liquid that is connected unambiguously with their concentration in the gas:

$$C_L^{lim} = \frac{Kf}{1 - AK} \cdot C_G \tag{2}$$

It is essential that the coefficient of proportionality should ve bery different from the thermodynamic partition coefficient, K, being either greater or less than K. When $AK > 0.5$, the method becomes inapplicable to the analysis of gases.

RESULTS AND DISCUSSION

The agreement between eqn. 1 and the experimentally observed dynamics of the accumulation of impurity is illustrated in Fig. 2, which depicts the saturation of pure acetic acid by trace amounts of aromatic hydrocarbons from air at 25° (ref. 7). The course of the dependence until one third of the ititial volume of the liquid (acetic
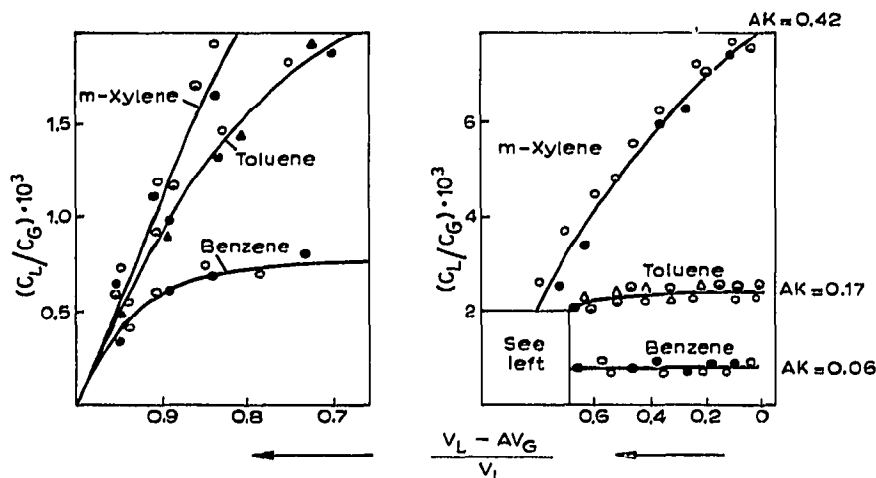
Fig. 2. Dynamics of the saturation of acetic acid with trace amounts of aromatic hydrocarbons from air at 25° [$AK < 0.5$; $K = C_L^{lim}/(fC_G + AC_L^{lim})$]. ●, Experiment 1; ○, experiment 2; ◐, experiment 3; ▲, experiment 4.

acid) has evaporated is shown on an enlarged scale on the left. In these experiments, the concentrations of each of the three aromatic hydrocarbons ranged from 10^{-7} to 10^{-5} mg/l, the initial volume of acetic acid from 1.5 to 5.0 ml and the carrier gas flowrate from 200 to 400 ml/min. The experimental points are seen to agree well with the theoretical curves calculated from the vapour pressure of acetic acid at 25° and the coefficients of distribution of aromatic hydrocarbons between air and acetic acid.

The agreement between theory and experiment for the case when $AK > 0.5$ is illustrated in Fig. 3, which shows the saturation of pure water by phenol present in air. This situation is unfavourable for the determination of trace amounts of phenol. Indeed, at 60° the curve does not reach a constant level because the
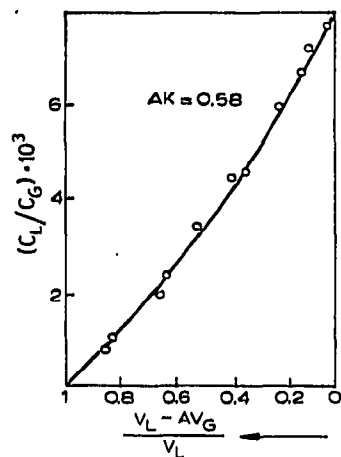

Fig. 3. Dynamics of saturation of water with phenol from air at 60° ($AK > 0.5$).

volatility of phenol is too low while that of water is too high at this tempera-
ture. If, however, we change the conditions of concentration (by reducing the volatility
of the absorbing liquid) in such a way as to meet the requirement $AK < 0.5$, the curve
for phenol will also reach the steady-state limiting concentration C_L.

Thus, a proper selection of the absorbing volatile liquid may make possible the
trace analysis of substances in air by the gas chromatographic determination of their
limiting concentration in the absorbing liquid, C_L^{lim}, with subsequent calculation of
their concentrations in the gas under analysis by the simple equation

$$C_G = \frac{1 - AK}{Kf} \cdot C_L^{lim} \tag{3}$$

With some additional limitations on the magnitude of A and K, the simple
equation of the partition law yields sufficiently precise results:

$$C_G = C_L^{lim}/K \tag{4}$$

We used this technique in the determination of simple aromatic hydrocarbons,
carbonyl compounds and diethylamine in air at the minimum detectable concentration
level (0.1–1 mg/m^3). With aromatic hydrocarbons, pure acetic acid was used as the
absorbing system[8,9]. The results of check analyses are presented in Table I. In a similar
way, one can analyze trace amounts of carbonyl compounds in air by trapping them
in water[8] (Table II). Table III gives results on the determination of diethylamine in
air by the gas chromatographic analysis of water saturated with this polluted air[7].

More detailed information on the selection of optimum stationary phases and

TABLE I

TRACE DETERMINATION OF AROMATIC HYDROCARBONS IN AIR BY EQUILIBRIUM
CONCENTRATION

Hydrocarbon	Amount introduced (mg/m³)	Amount found (mg/m³)	Analytical error	
			Absolute (mg/m³)	Relative (%)
Benzene	0.61	0.59	−0.02	3.3
	1.32	1.41	+0.09	6.8
	4.31	4.57	+0.26	6.0
	14.30	14.20	−0.10	0.7
Toluene	0.37	0.38	+0.01	2.7
	0.78	0.81	+0.03	3.8
	0.84	0.84	0	0
	8.0	7.70	−0.30	3.7
m-Xylene	0.11	0.12	+0.01	9.1
	0.38	0.37	−0.01	2.6
	2.00	2.00	0	0
	2.90	2.98	+0.08	2.8
			Mean	3.5

TABLE II

TRACE DETERMINATION OF CARBONYL COMPOUNDS IN AIR BY EQUILIBRIUM CONCENTRATION

Carbonyl compound	Amount introduced (mg/m³)	Amount found (mg/m³)	Analytical error	
			Absolute (mg/m³)	Relative (%)
Acetone	1.63	1.76	+0.13	8.0
	3.73	4.03	+0.30	8.1
	3.79	3.66	−0.13	3.4
	37.80	37.10	−0.70	1.9
Methyl ethyl ketone	0.55	0.57	+0.02	3.6
	1.29	1.40	+0.11	8.5
	2.44	2.38	−0.06	2.5
	30.80	31.20	+0.40	1.3
Methyl propyl ketone	1.06	1.09	+0.03	2.8
	1.08	1.16	+0.08	7.4
	1.54	1.33	−0.21	13.6
	11.50	11.20	−0.30	2.6
Acetaldehyde	7.65	7.82	+0.17	2.2
	8.00	7.70	−0.30	3.8
	65.20	71.50	+6.30	9.7
	65.20	59.00	−6.20	9.5
			Mean	5.6

conditions of chromatographic analysis, providing for the separation of a large excess of acetic acid or water in the determination of trace amounts, can be found in the literature[7,8,10].

CONCLUSION

The proposed method of determining impurities in gases can, to a certain extent, be considered as a "reversed head-space analysis". This technique will probably

TABLE III

TRACE DETERMINATION OF DIETHYLAMINE IN AIR BY EQUILIBRIUM CONCENTRATION

Amount introduced (mg/m³)	Amount found (mg/m³)	Analytical error	
		Absolute (mg/m³)	Relative (%)
0.91	0.89	−0.02	2.2
2.00	1.95	−0.05	2.5
2.54	2.70	+0.16	6.3
2.92	3.20	+0.28	9.6
4.70	4.64	−0.06	1.3
4.70	4.44	−0.26	5.5
60.40	62.70	+2.30	3.8
61.60	55.30	−6.30	10.2
		Mean	5.2

have wide application. Rather than being only a method of concentrating impurities, it can be used successfully in order to collect information on substances contained in air for subsequent processing.

The proposed method requires further study. In particular, one should consider the possibility that when determining impurities in humid air with the use of organic liquids with a high solubility for water, the partition coefficient may be non-constant because of a gradual increase in the water content in the absorbing liquid.

The equilibrium accumulation in volatile liquids appears to be promising for the collection of samples of unstable compounds that can readily oxidise, decompose or interact with the material of the equipment.

REFERENCES

1 A. G. Vitenberg, B. V. Ioffe and V. N. Borisov, *Zh. Anal. Khim.*, 29 (1974) 1795; *Chromatographia*, 7 (1974) 610.
2 J. Novák, V. Vašák and J. Janák, *Anal. Chem.*, 37 (1965) 660.
3 M. Selucký, J. Novák and J. Janák, *J. Chromatogr.*, 28 (1967) 285.
4 J. Gelbičová-Růžičková, J. Novák and J. Janák, *J. Chromatogr.*, 64 (1972) 15.
5 A. Dravnieks and B. K. Krotoszynsky, *J. Gas Chromatogr.*, (1966) 367.
6 A. G. Vitenberg, M. A. Kuznetsov and B. V. Ioffe, *Dokl. Akad. Nauk SSSR*, 219 (1974) 921; *Zh. Anal. Khim.*, 30 (1975) 1051.
7 V. N. Borisov, B. V. Ioffe and A. G. Vitenberg, *Zh. Anal. Khim.*, 30 (1975) No. 8.
8 B. V. Ioffe, A. G. Vitenberg and V. N. Borisov, *Zh. Anal. Khim.*, 27 (1972) 1811.
9 B. V. Ioffe, A. G. Vitenberg and V. N. Borisov, *U.S.S.R. Pat.* 428,245; *Bull. Inv. (U.S.S.R.)*, No. 18 (1974) 114.
10 A. G. Vitenberg, V. N. Borisov and V. A. Isidorova, *J. Chromatogr.*, 104 (1975) 51.